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Milo S.

1894

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The Brides of Manganese Formed by
Spontaneous Decomposition of the Man-
ganese Dioxide, Prepared by Treating Man-
ganous Sulphate with Potassium Per-
manganate.

and

The Reduction of Potassium Perman-
ganate by Manganese Dioxide Prepared
in the Wet Way.

Dissertation

^{Submitted}
~~Presented~~ to the Board of Univers-
ity Studies of the Johns Hopkins Uni-
versity for the Degree of Doctor of Phil-
osophy.

by
Milo S. Walker

1894.

67089

Acknowledgment.

The author desires to express his sincere thanks to Professor H. S. Morse who suggested and guided this work; also to Professor Ira Remsen for his instruction and valuable assistance during the time spent in his laboratory. He is also indebted to Professor Williams and Dr Ames for instruction in his subordinate studies.

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Introduction.

This work on the decomposition of ferrocyanide ferromanganate of manganese dioxide is a continuation of the investigations of Hues and Hopkins which were carried on in the laboratory during 1871-72 and are described fully in Hopkins' dissertation.

The work on certain hydrated oxides of manganese which contain small amounts of ferrocyanide was suggested by the marked instability of the so-called manganese dioxide obtained by precipitation when manganous sulphate is added to an excess of

potassium permanganate according to Vothhardt's method for preparing pure manganese dioxide.

The Higher Oxides of Manganese.

The higher oxides of manganese prepared in the wet way have been investigated by a number of chemists and carbon hydrated oxides containing more oxygen than Mn_2O_3 and less than MnO_2 have been reported. The views of chemists vary in regard to these supposed intermediate oxides. Some regard them as oxides of definite composition and others think they are mixtures of MnO_2 and other oxides of manganese.

Even in some cases it seems quite probable that mixtures have been analyzed and mistaken for compounds, but the fact should not be disregarded that there has been some very careful work by skillful chemists, which tends to show that there are certain comparatively stable forms of $\text{MnO} \cdot \text{Mn}_2\text{O}_3$ & Fe_2O_3 .

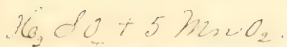
- It is suggested that the causes of the discrepancies of results in the work of different chemists in this field are - (1) The methods of analysis differ in accuracy, and none are sufficiently exact to determine the true relation of manganese to oxygen.
- (2) The oxides were prepared in different ways and subjected to

different treatment. It has been ascertained in the laboratory that changes of concentration and moisture will influence laboratory values about the combination of Doses of the higher oxides of manganese to a surprising extent. A dry oxide should not be allowed to stand in a working room or in a closed desk.

The Manganese Oxide Used in this Investigation.

The oxides were precipitated in the same way as those used by Morse and Hopkins and were prepared according to the following reaction—





A solution containing a known quantity of manganese sulphate was added to a solution containing more permanganate than was required to precipitate all manganese in manganese sulphate as Mn_2O_3 . Before precipitation an amount of nitric acid equivalent to the potassium in the permanganate was added. The precipitation was generally made at 65°C ., but in this work the acids were heated at different temperatures and in the presence of different amounts of nitric acid.

It is generally agreed among chemists who have worked in this field that the best way to

precipitated oxide contains manganese and oxygen in the ratio of manganese dioxide and this dioxide always contains ferrous iron.

It has not been ascertained that the spontaneous decomposition of this oxide has ever been investigated, but the fact that it is unstable has been noticed. It was found in this investigation that the instability of this dioxide is quite considerable. This suggested the present investigation to determine the spontaneous decomposition of the precipitated oxide under different conditions.

Method of Analysis

An adaptation of the Volhard method for the determination of manganese was used and was found to be very satisfactory. The method is volumetric throughout and it is not necessary to use a balance.

The burette require special attention. The rest of the apparatus may be of the ordinary type. Three burets are generally used. It is not necessary that they should be calibrated to any fixed system of weights and measures but it is very important that the relation of the calibration of one to the other should be known to a small fraction of the smallest division.

One of the burets is used for a solution of ceric and is for

potassium tetroxalate and the others
for potassium permanganate. These
solutions are generally made up
so 10 c.c. potassium tetroxalate would
reduce 10 c.c. permanganate. But it
is sometimes necessary in order to
secure greatest accuracy, to make the
solution of tetroxalate stronger than
the permanganate.

Dilute solutions of permanganate
and tetroxalate are used be-
cause they are more stable and
convenient. It is better not to have
the permanganate solution stronger
than 2.5 g. per liter.

The following example is given
to illustrate the method of analysis.

The solutions of permanganate

and tetroxalate were nearly equivalent. — 50 cc. tetroxalate = 50.15 cc. permanganate.

The oxide of manganese to be analyzed was standing under water.

Some of the oxide was taken out of the water with a porcelain spoon and immediately put into a 200 cc. beaker and 50 cc. tetroxalate added from a burette. Then about 10 cc. of a 20% solution of sulphuric acid was added. The contents of the beaker were stirred and heated to 60° until all the oxides had disappeared and the solution remained perfectly clear.

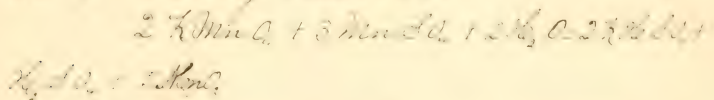
Then the excess of tetroxalate, which remained unoxidized was

18
determined by permanganate and it was found that 2.15 cc. permanganate were required. It is evident then that the unknown amount of the unknown oxide had as much available oxygen as 7.0 cc. of the permanganate solution.

The next step was to find out how many cc. of the permanganate solution would be required to precipitate all the manganous manganese in the solution in the beaker. The contents of the beaker were washed into a 1200 cc. Florence flask and diluted to about 500 cc. About 5 g. zinc sulphate and a few drops of nitric acid were then added and the solution heated to boiling. The flask was removed from

the fumes and permanganate was
quickly added from the burette
until the solution above the pre-
cipitated oxides had a slight rose
color which did not change after
the flask had been shaken several
times; 85.68 cc permanganate were
required to produce this color.

Having thus obtained the man-
ganese and available oxygen in
terms of volume of permanganate
solution the amount of manganese
manganese introduced into the te-
traxallate solution by the oxides may
be calculated upon the basis of
the following ^{ana} reaction:



But from the 85.68 must be

deducted the amount of permanganate required to precipitate all the manganese which was introduced by the permanganate used in analyzing the excess of lithiate.

Suppose 3 cc. KMnO_4 are reduced to the manganous state. It would require 2 cc. of the same permanganate solution to precipitate all manganese as MnO_2 ($2\text{KMnO}_4 + 5\text{MnO} + \text{K}_2\text{O} + 5\text{MnO}_2$)

$\therefore$ In the analysis which has been considered the volume of permanganate solution required to precipitate all the manganous iron introduced by 2.5 cc. permanganate, which was used in analyzing excess of lithiate is eliminated as follows,—

$$2.15 \times 3 \div 2 = 1.42 +$$

$85.68 - 1.42 = 84.25 = \text{no. cc. KMnO}_4 \text{ required to precipitate all manganous manganese.}$

The rest of the calculation is based upon the following facts, -

- (1) One molecule of KMnO_4 contains 2.5 atoms of available oxygen.
- (2) One molecule of MnCl_2 contains 1 atom available oxygen.

Therefore a solution in which X cc. of tetroxalate have been oxidized by MnO_2 will contain 2.5 times as much manganous manganese ^{as} one in which permanganate was the oxidizing agent. In this determination it was found, as stated, that the available oxygen in the amount of the side beam was equal to

the available oxygen in 48 cc. of the permanganate solution. Then if the 'mule' had been there would have been 2.5 times the amount of manganese in it as in 48 cc. of the permanganate solution. So in order to find how much permanganate was required to liberate all the manganese in MnO_2 , in case the mule was MnO_2 , this calculation was made.

$48 \times 2.5 \div 3 \times 2 = 80 = 80 \text{ cc. permanganate}$
required to liberate all manganese which had been in the mule if the mule was MnO_2 . But it actually required 84.25 cc. potassium permanganate.

From this 2 cc. must be deducted for it requires about that amount of that particular strength

of permanganate to produce discernible color in 500 cc. water;

So instead of 80 cc. as required.

For the 100 cc. now found, it is evident that the relation of manganese in MnO_2 is to the relation of manganese in the oxide considered as -

$$80:84.05 = 100:105.06$$

Now the relation of manganese to available oxygen in $MnO_2 = 100:100$ it is evident the oxide analyzed contained less available oxygen than MnO_2 or it may be said it contained more manganese than MnO_2 . If it is represented as the ratio of manganese usually are, it may be written $5 MnO:100 MnO_2$ or $MnO:20 MnO_2$ or Mn_2O_3, O_4 .

The calculation of the relation

of manganese to oxygen is much simplified by the use of a formula deduced as follows—

Let X = procc. permanganate equivalent in available oxygen to the oxide taken.

By use of this ^{two} manganese equivalent to precipitate all the manganese contained in the oxide as MnO_2 .

It is evident that $X \times 2.5 \times 2 \div 3 = X \div 0.6$. Thus if the oxide is MnO_2 $X = 0.6$.

The relation of MnO to available oxygen is $MnO : O = 55 : 8 = 1 : 0.145$. In the same way the relation of FeO to O expresses the relation of MnO to available oxygen in any compound of manganese and oxygen. The tables P. 339 are calculated according to the equation $145 : 100 :: 1 : (X)$.

In the preceding analysis

$2 = 4.8$ then $16 = 80$

$16 = 84.05$

'From this by the above calculation the relation MnO to $O = 1:9518$

Cal. for MnO_2 to $MnO_2 = 1:9523$

Having thus shown by an analysis actually made that the relation of manganese to oxygen can be readily obtained, it is necessary to add only a little to what has been already said about the method of analysis.

A beginner generally finds some difficulty in using this method, but all the difficulties can be overcome by practice and, if the weights are accurately calibrated, the results are remarkably con-

cordant, considering the amounts of liquid measured.

After some work-practice it is not difficult to make fairly accurate determinations which do not vary more than .1 cc. when 80 or 90 cc. of ferri-manganate are needed to precipitate all the manganese.

Suppose the oxide in the example given was, $MnO\ 19.5\ Mn_2O_3$, instead of $Mn_2O_3\ 100\ MnO$. This oxide would require .9 cc. more ferri-manganate to precipitate the manganese as MnO_2 which is a difference in this case of a little less than 10% of manganese in the oxide. It can be readily seen that in an oxide whose Fe_2O_3 can be easily determined if it is a whole number less than 50.

Further determinations can be made in some hours when accurate results are demanded. Approximate results require less time.

Preparation, Treatment and Analysis of Oxides

Oxide I. Prepared Feb. 18, 1893
About 20g. manganese sulphate were dissolved in 1 L. & nitric acid. This was heated to 65° and poured slowly into an excess of potassium permanganate dissolved in 500 cc. & nitric acid and heated to the same temperature. After settling upon a tilt plate as white as the precipitate was washed with warm water until the wash water showed no traces of sulphuric

acid or permanganate.

Without drying, the relation of oxygen to manganese was determined and found to be the same as in MnO_2 .

The remainder of the precipitated manganese dioxide was removed to a room not occupied as a working room and allowed to stand on a porous drying plate until dry to the touch.

The ratio of oxygen to manganese was determined as usual. These analyses are shown under the heading No. 1, P. 36.

For six weeks it lost oxygen slowly until it reached the composition $MnO_{20}MnO_2$ where it remained constant two weeks until June 13. It was then put into a beaker and covered with a watch glass.

As the laboratory was closed during the summer months, no determinations of manganese and oxygen were made until Oct. 2, '93 when it was found to have lost oxygen until the relation $\text{MnO} : 2 \text{MnO}_2 : \text{Mn}_2\text{O}_3 : \text{O}_2$ was reached.

Analyses made Jan. 18, 1894 and March 14, '94 showed no change in the oxide remaining in the beaker. But a portion taken out of the beaker Oct. 12 '93 and placed under water took up oxygen and determinations made Jan. 18 and March 15 '94 showed that it had taken up oxygen until its composition was $\text{MnO} : 15 \text{MnO}_2$. See table 2, 38.

Grade II Prepared as I except it was precipitated at 70°. Then freshly

Precipitated, the ratio of Mn to O was found to be MnO_2 . Treated like 101. It lost oxygen and in eight weeks had reached the constant composition $\text{MnO}_{20}\text{MnO}_2$ See No. 2 in table P. 36. During the summer it lost oxygen like 1 and a portion placed under water Oct 12 '93 took up oxygen like portion of 101 which were similar by heated, until its composition was $\text{MnO}_{20}\text{MnO}_2$. See table P. 38.

Oxide III Precipitated at 80° . The ferric sulphate and manganous sulphate were dissolved in 200% nitric acid and these solutions were made quite concentrated. The precipitate was washed with a dilute solution of potassium permanganate and then with water. Immediately after washing the ratio of Mn and O was the same as in MnO_2 ; but twenty-four hours later a portion of this same oxide left

exposed to the air, was about $\text{MnO}_{0.3}\text{MnO}_2$, and another portion standing under water was nearly $\text{MnO}_{1.00}\text{MnO}_2$.

The portion standing exposed to the air lost oxygen like No. 1 & 2 and in 5 weeks was $\text{MnO}_{0.20}\text{MnO}_2$ and remained in that condition six weeks, until the laboratory was closed for the summer. See No. 1 in table 93. Analyzed at the end of the summer, it was found to have changed ^{to $\text{MnO}_{1.25}\text{MnO}_2$} like No. 1 & 2 and remained at that composition until March 15, '94, when the last analysis was made.

The portion placed under water lost oxygen more slowly, but in eight weeks it also reached the composition $\text{MnO}_{1.25}\text{MnO}_2$ and retained that composition from Apr. 29, '93 to March 15, '94, when the last analysis was made.

Oxide IV. Prepared at 80° in a solution of H_2SO_4 acid. About 200g. of MnO_2 were prepared and washed for five days with strong solution of potassium permanganate. In order to keep the dioxide constant over night it was to keep a sufficient amount of permanganate in the water. Large amounts of this manganese dioxide decompose permanganate rapidly and the dioxide begins to lose oxygen immediately if allowed to stand free from permanganate.

This oxide was analyzed immediately after washing free from permanganate and was found to be MnO_2 . But after it had stood twenty hours on a drying plate, it was found to be MnO or Mn_2O_3 . The was heated into

several portions and heated in various ways.

Portion No 1 was allowed to stand in a covered porcelain dish. In four weeks it was $MnO_{2.0}MnO_2$ and remained there four weeks until the laboratory was closed. During the summer it lost oxygen going to $MnO_{1.25}MnO_2$ like No 1, 2 & 3 and in every other respect behaved like them. It is designated water in table 237.

Portion No 2 heated in an air bath to 65° it immediately lost oxygen and in a few hours it was $MnO_{1.25}MnO_2$ and remained constant for some time, but after continued drying and warming it lost more oxygen until it reached the composition about $MnO_{0.75}MnO_2$. It did not remain constant there.

It quickly took up oxygen on exposure at ordinary temperatures until it reached a composition $MnO_{1.5}MnO_2$, which remained constant.

These experiments were repeated several times and always with the same result.

Sometimes the oxide was heated as high as 130° but the result was the same as at lower temperatures.

On the basis of a large number of experiments, it was found that $MnO_{2.0}MnO_2$ is so sensitive to slight differences in temperature and moisture that if the dry oxide is heated 15 minutes in the air bath it often changes to $MnO_{1.25}MnO_2$. And if that oxide is afterwards allowed to stand exposed to the air, at ordinary tempera-

been in contact it is MnO₂ but
in no case has it been observed that
an oxide which has lost oxygen, so
^{that} its composition is less than MnO_{1.5} &
MnO₂ can take up more oxygen than
is required for MnO_{1.5} MnO₂.

It seems that the temperature
at which dry MnO₂ MnO₂ breaks down
when exposed to the air somewhere
between 20+30° but it breaks down
more rapidly at higher temperatures.

The oxide MnO_{1.5} MnO₂ is still more
sensitive to warm dry air than MnO₂. But either of these can be boiled
in water without undergoing change.

When a specimen of the oxide was
heated to 200° for four hours and it
lost oxygen until it was MnO_{0.75} MnO₂
and when this was moistened it changed

ed to $MnO_{10}MnO_2$. But during the summer it lost oxygen until it was $MnO_{7.5}MnO_2$. It remained constant at this composition from Oct. 4, '73 to March 20, '74 at which time the last analysis was made. This is the only experiment that was tried in this way.

Portion No. 3. A portion of the oxide dried on a plate until it was $MnO_{20}MnO_2$ was divided into five parts. Each part was put into a small beaker and covered with a watch glass. Four of the beakers containing the oxide were placed in different parts of the building and the fifth was set in the open air outside the building. They were analyzed from time to time and it was noticed that the portions placed outside the building and over

in the sunlight and one in darkness
 in a room removed from the working
 rooms of the laboratory retained their
 composition MnO_2 . But a portion
 placed where a stream of air which was
 in daily use, lost oxygen slowly un-
 til ^{the composition} MnO_2 was reached and no
 further loss of oxygen occurred during
 the 4 weeks which it remained there
 after having reached this composition.
 The other portion was placed in a
 laboratory desk in a working room of
 the laboratory and it seemed to change
 constantly, sometimes gaining oxygen
 sometimes losing, but the total loss
 was greater than the gain and when
 analyzed 4 weeks after being placed
 there it was MnO_4 which was
 the last analysis made. It is

noticed repeatedly in other experiments that a dry oxide can not be kept, without undergoing change, in the part of the laboratory where work is carried on.

Oxide I. Precipitated by placing an H_2SO_4 acid solution of permanganate and manganese sulphate in the nitric acid were quite dilute. The freshly precipitated oxide was MnO_2 and from this MnO_2 , MnO , MnO_2 , MnO , MnO_2 and MnO were repeatedly obtained in the same way as from IV. No. 5 in table P. 37 and 5, P. 38 were obtained from this.

Oxide VI. Precipitated in a large volume of H_2SO_4 nitric acid.

A portion was exposed to the air like the portions of I, II, III, IV, & V. identical

ed in tables 9, 37. This fraction is No. 6 in this table.

Another portion of the MnO_2 was placed under water and in five weeks it reached the composition MnO_2 and remained constant at that composition 5 weeks then slowly changed until it again became constant at $MnO_{20}MnO_2$ where it remained from June '93 to March '94.

Grade VII. A mixture of oxides obtained from No. 1, 2, 3, 4, 5 and also some from those used by Messrs. Hopkins were heated with potassium permanganate until there was a perceptible evolution of gas, which is an indication that the oxygen resulting from the decomposition of the permanganate is

no longer required to oxidize the oxides to MnO_2 . The oxides were filtered and quickly washed free from permanganate and were found to have been completely reoxidized to MnO_2 . They were treated in the same way as to 25.5 re-oxidation in table P. and with the same result.

Oxide III Precipitated like IV

It was divided into nine portions. See P. 11.
 20g were placed in small crystallizing dishes ^{resistors} containing water
 10g " " " " " " " " " 10g
 10g " " " " " " " " " 10g
 10g " " " " " " " " " 10g
 10g " " " " " " " " " 10g
 10g " " " " " " " " " 10g
 10g " " " " " " " " " 10g
 10g " " " " " " " " " 10g
 10g " " " " " " " " " 10g

It was placed under water

It was desired to find whether the direct sunlight had any effect upon the composition of the oxides standing in resistors containing different drying

agents. So a, b, c, rd were placed in direct sunlight and a', b', c' and d' in diffused light.

The oxides when put into the desiccators and under water were wet and were all in the dihydrate state. They stood in the desiccators from June 1893 when they were analyzed and all except a and b were $MnO_{20}Mn_2$ and remained that composition until March '94, when the last analysis was made.

The determinations made Oct. 2. showed that a (one over water) contained an oxide $MnO_{12.5}Mn_2$. A determination of this oxide Jan. 13, '94 showed it had taken up oxygen and gave $MnO_{15}Mn_2$.

f, (over $CrCl_3$) during these intervals had taken up oxygen, ^{that} so from its composition $MnO_{10}Mn_2$ Oct. 2, it became $MnO_{12.5}$

[Faint handwritten text at the bottom of the page, mostly illegible.]

MnO above MnO_2 and remained at that composition until March 12 when the final analysis was made.

The change which it undergoes is in accordance with previous observations that at temperatures below 20° of moisture is present. MnO 12.5 MnO_2 takes up oxygen until MnO 15 MnO_2 is reached.

A part of $\frac{1}{2}$ was taken out of the desiccator and moistened. It took up oxygen, as was expected, until MnO 15 MnO_2 was reached.

Concluding Remarks

This investigation was undertaken with a view of obtaining some light upon the spontaneous changes which the manganese dioxide prepared from manganous

... and ...
undergoes under different conditions of
temperature, moisture, light.

In this work no account is taken
of the water and potassium which these
oxides undoubtedly contain.*

Different preparations of the dioxide
were made in order to show what difference
if any there is in the stability of the di-
oxide precipitated under different con-
ditions of temperature, concentrations
of solutions and amount of nitric acid
present.

The following tables* show there is
little if any, difference.

Mr. ...

*All the results given in these tables are the average
of two or more determinations made for each case.
Very minute differences were neglected.

2 113.

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1892-1893

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10. C. M. ...

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127.5 (m) 2.5m, 127.5

1. *Phlox*
 2. *Phlox*

Y. 200. 200. 200. 200

1891. 925-9

Cal. 1. 1251
D. 1. 87, 9

Cal. ii. 4228

Cal. 1. 9. 22
D. 1. 9. 22

174.11.1

Cal 1: 129

(21) 1. 237

22-

Cal. 1. 2, 4

Grand Lagoon, Feb. 10, 1900

Cal. 1. 7228

Sept 27

Feb. 1. 1920

It is further stated that there were eleven other experiments not included in the tables in which oxides of manganese were allowed to spontaneously decompose in the air. They all contained more oxygen than $MnO_{20}Mn_2$. Eight of these decomposed until $MnO_{20}Mn_2$ was reached and from that time there was no further loss of oxygen.

The remaining three were exposed in one of the winding rooms of the laboratory and none of them showed any tendency towards assuming a constant composition. They were probably affected by the laboratory vapors.

Some different oxides containing more oxygen than $MnO_{20}Mn_2$ but less than MnO_2 , were placed under water. In every case there was a loss of oxygen until the same constant composition $MnO_{20}Mn_2$

was reached.

General Statements.

1. $MnO_2 \cdot MnO_2$ is the ^{only} stable decomposition product when the manganese dioxide, prepared as previously described, is allowed to spontaneously decompose under water.

2. Showing the transition from the ^{stable} $MnO_2 \cdot MnO_2$ into the superoxide that now seems to be the final decomposition product in moist air.

3. Dry $MnO_2 \cdot MnO_2$ broke down into $MnO \cdot 12.5 MnO_2$ during the summer months.

4. Dry $MnO_2 \cdot MnO_2$ when gently heated breaks down into $MnO \cdot 12.5 MnO_2$.

5. When $MnO \cdot 12.5 MnO_2$ is moistened it oxidizes, in the air, to $MnO \cdot 15 MnO_2$.

Conclusions.

The following manganites of manganese have been described.

(MnO) MnO_2 has been obtained by treating $Mn_2Si_2 5\frac{1}{2} Si_2$ with much water - Frankland. *pr. Chem.* [2] 36. 461 & 36.

$MnO_2 MnO_2$ is formed by heating $MnCO_3$ in contact with the air. *Wissenschaft.* 1857

$MnO_2 MnO_2$ is formed by heating $MnCO_3$ with excess of Mn salts in presence of strong acids - Gorgeu Bull. *Chim.*

$MnO_5 MnO_2$ is obtained 1. By treating $MnCO_3$ with excess of Mn salts - Gorgeu Bull. *Soc. Chim.* 51. 2. By action of Chlorine water upon $MnCO_3$ - Gorgeu Bull. *Chim.* 51. 3. By precipitation with hydrogen superoxide on MnO_2 . Solution of manganese salts. *Bulletin Soc. Chim.* 3 I 1891

MnO11MnO₂ has been obtained by heating
MnO5MnO₂ in ²current of air - Vele, Soc.
Chem. Soc. 37 231.

By heating MnO5MnO₂ in a current of
oxygen MnO23MnO₂ was obtained - Vele,
Proc. Chem. Soc. 37 231.

The oxides found in this investigation
appear to be related to that best known of
all manganites MnO5MnO₂. For if the for-
mulae are doubled they form an homologous
series of oxides, four members of which are
certainly known, two probably exist and
one is not yet known.

- | | | |
|------------------------------|---|---|
| 1. MnO5MnO ₂ | = | (MnO ₂) 10 MnO ₂ |
| 2. MnO7.5MnO ₂ | = | (MnO ₂) 15 MnO ₂ |
| 3. MnO10MnO ₂ | = | (MnO ₂) 20 MnO ₂ |
| 4. MnO12.5MnO ₂ | = | (MnO ₂) 25 MnO ₂ |
| 5. MnO15MnO ₂ | = | (MnO ₂) 30 MnO ₂ |
| 6. MnO17.5MnO ₂ ? | = | (MnO ₂) 35 MnO ₂ unknown |
| 7. MnO20MnO ₂ | = | (MnO ₂) 40 MnO ₂ |

No. 1 is the well known oxide of Gorgeu concerning the existence of which there is no doubt.

No. 2 was formed according to the experience of the author when manganese oxide was heated on a steam pipe for a long time, but, as that composition was found to be constant, its existence seems probable. It was also found by exposing to the air at ordinary temperature an oxide derived from Mn_2O_3 and heated to 200° .

These two experiments indicate the existence of an oxide of such a composition.

No. 3 is doubtful and its existence requires confirmation, and as it has been reported by Gorgeu (Bull. Soc. Chim. 1875 &c.) to obtain it by treating MnO_2 with concentrated hydrochloric acid at 0° and adding to the supernatant.

digest a quantity of water at 0° when
a precipitate was formed which was
dried in the air but the composition
 $MnO_{10}MnO_2$.

An oxide of the composition $MnO_{10}MnO_2$
was obtained twice in this investigation
but it was unstable, and the experiments
have not been repeated. See p. 33-28

As is due to the influence of
the author, a sludge formed when the
manganese dioxide used in this inves-
tigation is dry and gently heated in
the air or when it is exposed to the air
during the summer.

No. 5 is formed by moistening No. 4
and exposing it to the air at ordinary
temperatures, or by allowing it to stand
under water.

No. 6 has not been obtained.

ing the course of this work, but it appears to have been found by another in this laboratory. It was formed by digesting MnO_2 with water and repeatedly evaporating to dryness in the water bath. But as the experiment was not repeated, its existence requires confirmation.

No. 7 was always obtained when the same yellow hydrate used in this investigation was allowed to spontaneously decompose in thin layers during the winter and spring months.

2. When the same orange hydrate is allowed to decompose in the presence of water, and, further, it seems that the presence of water prevents any change in the composition of $MnO \cdot 25MnO_2$ at any temperature below $100^\circ C$.

Decomposition of Potassium Permanganate by Manganese Dioxide.

A few years ago it was noticed in this laboratory that the decomposition of potassium permanganate solution is facilitated by ^{the} ~~the~~ addition of ^{the} ~~the~~ manganese dioxide. See Hopkins Dissertation 25 22.

It seemed desirable that subsequent observations should be made to determine (1) The stability of solutions of potassium permanganate, free from acids in the sunlight & direct light and darkness.

(2) The effect of the presence of acids & manganese under these conditions;

(3) The effect of varying amounts of manganese dioxide upon the same

solution.

The permanganate solutions used in this work were standardized with pure potassium tetroxalate¹

The permanganate was freed from the bottles through a filter into the bottles by an arrangement which allowed no particles of dust to get into the solution in the bottle or in the portion withdrawn for analysis.

Calibrated bottles were used.

The oxides of manganese used in this investigation were prepared as described. $P.P.O.$ dried at 65° . As this work was begun before the investigation of the oxide it is not understood what the relation of MnO_6O , was in these oxides. It is almost certain however, that it was not MnO_2 because

¹ The permanganate was a distillate through a glass filter and a silver filter.

all subsequent attempts to prepare
 Mn_2 in this way have failed, because
 the drying seemed to be accompanied
 by loss of oxygen until $MnO_{12.5}$ was
 reached. It is probable that the oxide
 was nearer $MnO_{12.5}$ than Mn_2
 when the reaction actually occurred.
 How can the reaction between manga-
 nese dioxide and potassium permanga-
 nate be studied when the reagent
 used is not manganese dioxide?

It has long been known that
 an oxide of manganese containing
 less oxygen than MnO_2 is converted
 to MnO_2 by potassium permanganate.
 It is evident that this oxidation is
 effected at the expense of the per-
 manganate, because the permanganate
 is rapidly decolorized under the

complete oxidation of the oxide to MnO_2 has been effected.

This is a very important consideration in this work, and for that reason it has been the subject of repeated experiments in this investigation. The results of these experiments without exception confirmed the view that an oxide, ^{prepared in the wet way} poorer in oxygen than MnO_2 is oxidized by even a dilute solution of permanganate to MnO_2 , and that the oxidation proceeds no further than MnO_2 . The minimum time required for this oxidation is probably not over three days, if an excess of permanganate is present.

So if an oxide containing less oxygen than MnO_2 is added to a solution of permanganate it would be ex-

tested that the permanganate solution
would lose strength until the oxide
is oxidized completely to MnO_2 . After
that has taken place the reaction
between the permanganate and di-
oxide can be studied. The following
calculated experiments were tried with
a view to finding whether, after the
oxidation of the oxide to oxide by per-
manganate solutions at ordinary tem-
peratures, there is a continuous reaction
between the permanganate and dioxide.

Experiment I. Two solutions of
potassium permanganate were care-
fully filtered through columns of
glass wool and asbestos. The first
solution was equivalent to 5 mg. in
an the former condition for use

of the second solution was equivalent to that of the first in the former solution, or nearly twice as strong as the first solution.

Eighteen liters of each solution were put into six many liter bottles. These bottles were carefully dried after having been cleaned with any strong solutions of potassium permanganate and sulphuric acid. They were closed with perforated rubber stoppers, through which we inserted small glass tubes bent at two right angles and drawn out to small openings at both ends. A small glass tube closed with a doubly-perforated cork stopper and containing a little potassium permanganate was slipped up the outer end until the surface of the potassium

ganate. so that it was near the opening of the tube leading from the bottle. The arrangement was adopted in order to leave the solution in contact with the air without danger of contamination by evaporation.

Into one half of the bottles containing the weaker solution and into one half the bottles containing the stronger solution of permanganate were put the dry oxide of manganese in carefully weighed portions of .5 g. each.

Then one third of the bottles were placed in the sunlight and arranged so as to get, as nearly as possible, the same amount of sunlight for each bottle of potassium permanganate. An equal number similarly arranged were placed in ~~sublight~~

placed bottle in the same room until
 we went on to the 10th house in
 the same room.

This experiment was begun Decr
 1872. The rate of decomposition was
 determined as follows: Every further
 days the strength of the permanganate
 in each of these bottles was determin-
 ed by a standard solution of ferrous
 and tetraoxide. The further bottles found
 subjected to other different conditions
 as to light, strength and presence or
 absence of oxides.

As would be expected from the
 facts given on p 47 there was a consid-
 erable loss of oxygen, ^{sometimes} during the first
 fourteen days in all the permanga-
 nate solutions standing in contact
 with the water. The decomposition

and about the same in solutions of the same strength in darkness and under diffused light. But in the sunlight the decomposition was somewhat greater; see Table 5.38.

In the solutions in which no oxide had been formed, no trace of a perceptible oxygen was observed in diffused light and darkness, but in the sunlight there was a perceptible loss, as shown in the table.

It can be safely assumed that the oxidation of the oxide in contact with the permanganate solution was complete by the time the per-

oxide is formed that the amount of the permanganate in presence of oxides during the first fourteen days is no indication of the effect of the

presence of manganese dioxide upon
potassium permanganate. In fact
the oxides are always found to be in
the Mn₂ state after heating much longer
than fuming stage, all observations
made upon the solutions after this
period must be regarded as observa-
tions upon potassium permanganate
solutions in contact with Mn₂.

The solutions were subjected
at intervals of fuming stage. The loss
of strength in each of the solutions
in the direct sunlight was much
greater than in any of those in
diffused light or darkness. In the
latter no loss whatever has been
seen in the solutions containing
no oxides of manganese. But in the
ones containing Mn₂ there was loss

... as the weather that it could scarcely be detected at short intervals and could be measured only at comparatively long intervals.

The following table shows the total percentage decomposition of these solutions

1.	From Dec 10, '92 - Dec 24, '92	} Portions taken for analyses were from the same bottles in suc. session.
2.	" " " " - May 31, '93	
3.	" " " " Oct 4, '93	
4.	" " " " March 16, '94	
5.	" " " " " " 17, '94	

The bottles had been left unopened from Dec. 10, '93.

Dec. 24 '42

the solutions from which portions were withdrawn from time to time for analysis. This may be largely due to the accumulation of oxides on the sides of the bottles, which may have the effect of shading the solution.

The oxides on the bottles from which portions were frequently taken for analysis were loosened from the sides by the opening and closing of bottles, thus probably producing an inequality between those and the other bottles as to the amount of sunlight which entered the solutions.

In the solution of *Calceolarius* for analysis its color in different light and darkness there was no composition when manganese dioxide was present, but no change whatever

could be detected in the solutions free from manganese dioxides.

Experiment II The object was to determine how a solution of potassium permanganate is acted upon by different quantities of MnO_2 .

Twenty four 500 cc. bottles each containing exactly 50 cc. of permanganate solution were stoppered and closed in the same way as before.

In the sunlight are placed two bottles and containing no oxide of manganese

b & b'	"	.25 g.	"	"	"
--------	---	--------	---	---	---

c & c'	"	.50 g.	"	"	"
--------	---	--------	---	---	---

d & d'	"	1.00 g.	"	"	"
--------	---	---------	---	---	---

e & e'	"	2.00 g.	"	"	"
--------	---	---------	---	---	---

f & f'	"	5.00 g.	"	"	"
--------	---	---------	---	---	---

Every fourteen days the strength

of permanganate solution in a, b, c, d, e of above determined as in Expt 1. But a', b', c', d', e', f' were allowed to stand from Feb 11 to 15 to Oct 5 '91.

At the same time an exactly similar series of experiments ^{was} started in which the solutions of the strength were placed in diffuse light. They were analyzed in the same way as in the sunlight as those in the sunlight.

As in Expt I, there was considerable decomposition of the solutions in contact with the water during the first two weeks which of course is explained in the same way as in case of Expt. 1. S.P. 1000.

The analyses following the one Feb. 25 '93 are not given because they

* See table 2

do not indicate the decomposition of permanganate by HNO_3 in a quantitative way for (1) There is frequent change of volume owing to the withdrawal of portions of permanganate for each analysis (2) The suspended manganese dioxide in the portion withdrawn for analysis is lost so it is impossible to calculate the loss of permanganate and hence in this case. But it was clearly shown that manganese dioxide does decompose potassium permanganate and, in the two determinations following the one given, the decomposition was nearly proportional to the amount of the manganese dioxide in the bottles.

The bottles into which are put $\frac{1}{2}$ g. of oxides contained no permanga-

nate after two months and in eight months the solutions in contact with Zn of the air are not notably free from permanganate.

The solutions a, b, c, d, and e, in the sunlight and a corresponding one in which but has attempt to be in different light were analyzed Feb. 7, '93.

The following table shows the total percentage decomposition of these solutions which had been left unaltered from Feb. 1, '93 to Feb. 5, '93 and the decomposition of ^{the} series in ^{and sunlight} diffused light _^ from Feb. 11, '93 to Feb. 24, '93.

Residue 2 1/2 lbs. 1000 1000 1000 1000 1000

1000 1000	Unoxidized	58	3.23	6.17	13.56	26.45	52.3
	Unoxidized		1.72	5.78	11.42	24.83	53.87
1000 1000	Unoxidized	23.67	39.95	31.80	39.65	61.37	1000 1000
	Unoxidized	1	4.27	14.75	29.26	59.47	

It can be seen from the above that the oxides are oxidized to the dioxide before further change after starting the experiment. As in the different light the loss of available oxygen from Feb 25 to Oct 5 must be due to the contact of the ferromagnets with oxygen in the air. It will be seen that the decomposition in different light is nearly

proportional to the amount of the oxides present, except in the case of .25g and 5g. But in making such close distinctions the liability to experimental error is such that the best results cannot be selected in this work.

As the somewhat anomalous results are to be expected, for a coating of MnO_2 is formed upon the sides of the bottles which must have the effect of shading the solutions.

Results in the Bottles after the Oxidation has Proceeded nearly to the End.

The ratio of MnO_2 to O in the oxides was determined in six of the bottles before the color of the permanganate had

entirely disappeared and it was found
to be MnO_2 in every case.

	Calculated	Found
No 1.	1:1	1:1.999
No 2.	1:1	1:1
No 3.	1:1	1:1
No 4.	1:1	1:1.999
No 5.	1:1	1:1.001
Ave	1:1	1:1.000

But when ^{the} ratio of MnO to O was
determined in these cases after com-
plete decolorization of the permanganate
in the solution had taken place
and in no case was MnO_2 found. The
results varied from MnO to MnO_2 to
and 39.7 MnO_2 .

There is nothing in this work that
indicates the final decomposition pro-
ducts of the residual manganese dioxide.

in these bottles, but it is certainly shown that they are unstable although their decomposition is much slower than that of the highly precipitated manganese dioxide. This latter fact makes the study of their spontaneous decomposition more difficult.

The instability of these hydrates is due to their reduction from their decomposition products to MnO_2 at the expense of the potassium permanganate with which they are in contact was suggested in Hopkins's dissertation as the partial explanation of the decomposition of $KMnO_4$ by MnO_2 .

See Hopkins's dissertation P. 24.

The supernatant liquid above the oxides after the color of the

Permanganate had entirely disappeared
 and contained small quantities of
 a substance in solution the nature
 of which could not be determined.
 It contains a small quantity of
 manganese, has oxidizing properties
 and appears to contain considerable
 potassium. Its solutions do ^{not} show
 alkaline reaction with organic indi-
 cators, but, if evaporated to dryness on
 the water-bath, it evidently decomposes,
 for if the residue is moistened the so-
 lution becomes strongly alkaline.

It seems that the potassium of
 the decomposed permanganate is partly
 in the residue and partly in the sub-
 stance in solution. Caustic potash
 was found in any of the solutions in
 the bottles.

The results of this investigation indicate.

(1) Aqueous solutions of potassium permanganate are decomposed by manganese dioxide, prepared in the ^{usual} way, and the decomposition is proportional to the amount of the dioxide present.

(2) Solutions of permanganate decompose when placed in the sunlight as all who have tried this experiment agree.

(3) Solutions of permanganate of 5 or 10 mg. Fe are stable in diffused light or darkness, if care is taken to filter off all the acids of manganese before the solution is put away.

The ordinary laboratory solution of permanganate, although completely

gallium is not entirely stable this
is probably due to the particles of dust
and scales of manganese which drop
into the bottle when it is frequently
opened.

Influence of the Presence of Manganous Salts on the Oxidation of Oxalic Acid and Formic Acid by Potassium Permanganate.

Some one who has had experience in titrating oxalic acid with potassium permanganate has noticed that in order to secure rapid and complete reduction it is necessary to heat the solution before the permanganate is added. But after a little permanganate has been added the reduction proceeds easily and rapidly even when the solution is cold.

The presence of manganous salts seems to be the only difference in condition after the addition of permanganate. It has been suggested by different

chemists that manganous salts act as carriers of oxygen between ferrous salts and a reducing agent. Thus when tolerable traces of ferrous salts are added to a solution of ferric salts precipitates oxides which are said to vary in composition from Fe_2O_3 to FeO . These oxides are very readily reduced by oxalic and formic acids and it is probable that the breaking down of the ferromanganate by the manganous salts in solution affords a good opportunity for complete reduction of any reducing agents present.

If this explanation is correct then the presence of manganous sulphate in the solution should inhibit the reduction of oxalic or formic acid by permanganate. To determine whether

was a little manganese which
was added to a solution of potassium
tetroxide and sulphuric acid and it
was found that it readily reduces per-
manganate even in the cold. Similar
experiments were tried with formic
acid and with similar results. Solutions
containing oxalic or formic acid and
either manganous chloride and hydro-
chloric acid or manganous sulfate
and nitric acid, act the same way.

In order to ascertain whether it is
practicable to use manganous chloride
in analysis a variety of experiments
were tried.

A number of comparative titra-
tions of potassium tetroxide and
potassium permanganate were made
in order to determine whether the

is any difference when the determination is made in the usual way, ^(by heating to 65°) or when manganous sulphate is added to the solution before titrating. Varying amounts of manganous sulphate were used and titrations were made at temperatures ranging from 10° to 65°C. and no difference whatever was noticed between those results and those obtained when the solution of tetroxalate was simply heated to 65°, sulphuric acid added and titrated in the usual way.

When a considerable amount of manganous sulphate is present the KMnO_4 must be added very slowly and with constant stirring, otherwise the solution becomes yellow from the action of the permanganate

upon the manganous manganese and a loss of available oxygen is shown by the high results then obtained.

The same error, but to a less extent, is introduced in estimating oxalic acid in the usual way if the permanganate is added fast enough to keep the solution colored.

The error is generally slight but carelessness in regard to this may produce a difference of 5% when 10% of oxalic acid strength of oxalic acid and permanganate are used.

In all cases where manganous sulfate was added, the end reaction was somewhat obscure owing to the precipitation of oxides when the least excess of permanganate was added.

The best results were obtained

when the permanganate was titrated into a 200 or 300 cc. beaker containing about 100 cc. of the solution of oxalic acid or tetrapotassium manganous sulphate and sulphuric acid. White glazed paper was placed on three sides and beneath the beaker.

The readings were taken when there was just enough permanganate to produce a slight permanent pink color or the characteristic manganate color. The results thus obtained were much better than when it was attempted to titrate to a permanent "Titrations to color" is subject to certain errors that need not be enumerated here.

In the following comparative determinations two calibrated bottles

These results and others, not as carefully worked out show that

1. By taking very great care it is possible to get fairly concordant results even to the second decimal of a cc.

2. The presence of manganese sulphate in the solution does not affect the accuracy of the titration.

Several experiments were made to test the practical application of manganous sulphate in the reduction of oxalic acid at temperature below 60° and the following methods were found satisfactory.

Dissolve 50g. manganous sulphate in about 1 l. of water.

For temperature 15° - 30° C. and strength of permanganate by a less kind and 100 cc. 0.005% solution and 100 cc. 20%

solution sulphuric acid and 60cc. water to 20cc. oxalic acid.

For the same solutions of oxalic acid at temperature above 70°C . use 1cc. of the sulphate and 5cc. of the sulphuric acid solution and 60cc. of water.

The following is recommended as the best practical method when the solutions can be heated to 50° without danger of decomposition or loss.

Heat 20cc. oxalic acid, diluted with 80cc. water, until it begins to feel hot to the hand ($40^{\circ}-50^{\circ}\text{C}$). Then add 1cc. of the manganous sulphate solution and 5cc. of sulphuric acid solution and titrate with permanganate.

A few preliminary experiments

were tried with uranium as a carrier of oxygen but they were not carried far enough to give definite results.

Conclusion

It appears that the observed increase in the rate of the reaction of permanganates upon oxalic acid and formic acid is due to the action of the manganese manganese as a carrier of oxygen.

Biographical Sketch.

Wilo Scott Walker was born at Mus-
dock Ohio Feb. 16. 1867. He was a student
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